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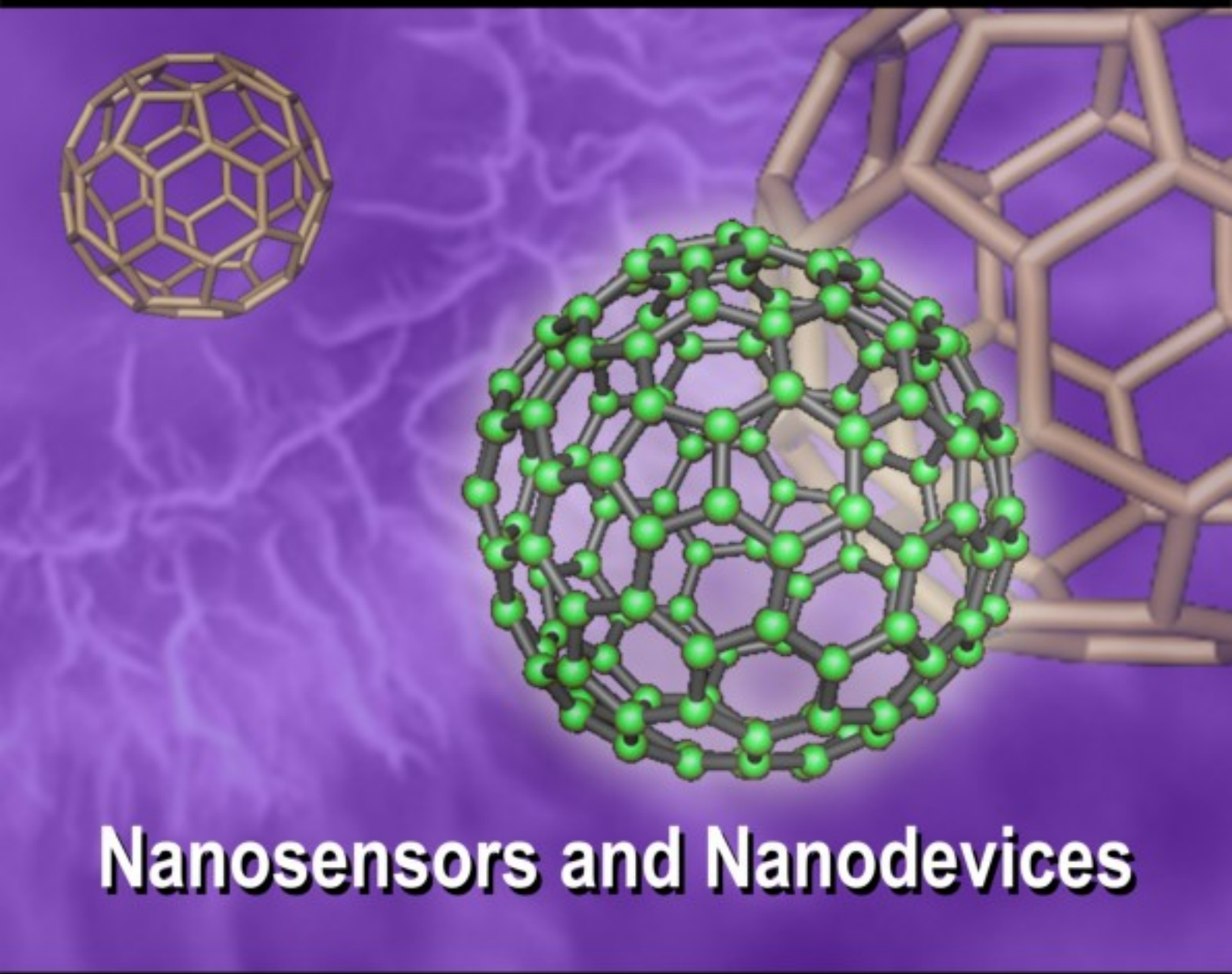

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Contents

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Palladium Surface Modification of Nanocrystalline Sol-Gel derived Zinc Oxide Thin Films and its Effect on Methane Sensing

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Abstract: Nanocrystalline n-ZnO thin films were deposited on SiO_2-coated p-Si substrates by a sol-gel method to fabricate ZnO-based resistive sensors. Two types of sol-gel ZnO based sensor structure, one as deposited and other with surface modified by palladium were investigated for methane sensing. The response magnitude, response time and recovery time were studied in the temperature range of 100-350 °C and at methane concentrations of 0.01 %, 0.05 %, 0.1 %, 0.5 %, 1 % and 1.5 % for both the sensor structure. The Pd modified sol-gel ZnO based sensor was found to provide lower operating temperature (150 °C), lower response (recovery) time, higher response magnitude and higher sensing range for methane compared to its earlier reported unmodified counterpart (250 °C). With Pd modification ZnO was found to sense methane concentration as low as 0.01 % and as high as 1.5 % whereas for unmodified one this range was restricted between 0.1 % to 1.0 %. *Copyright © 2009 IFSA.*

Keywords: Nanocrystalline Zinc Oxide, Sol-gel**,** Pd surface modifier, Pd (Ag) catalytic contacts, Methane detection

1. Introduction

Detection of lower concentration of methane at a lower temperature is extremely desirable for mining environment [1]. Moreover higher concentration like as high as 5 % should also be efficiently detected as in the mining environment methane concentration is high in general. Semiconducting metal oxide nanostructures elements can be configured as resistors whose conductance can be modulated by charge transfer across the surface or as a barrier junction device whose properties can be controlled by applying potential across the junction [2-4]. Modification of the surface further offers a possibility to improve their sensing ability.

Low temperature methane detector using nanocrystalline ZnO with Pd and other noble metals like Rh, Pt as the catalytic metal contact on the metal oxide surface[5-7] were reported earlier having the sensing temperature 220 °C and 250 °C depending upon whether the ZnO sensing film was grown electrochemically or by a sol–gel method, respectively. Recently P. K. Basu, et al [8] reported on Low temperature methane sensing by electrochemically grown and surface modified ZnO thin films where the operating temperature is in the range of only 70 °C to 100 °C with appreciably fast response and recovery time.

But the problem with such electrochemical process is that they are not compatible to standard CMOS fabrication process as the entire sensor platform has to be dipped into Oxalic acid solution for electrochemical anodization [8]. But as in case of sol-gel process due to drop and spin method it offers good handshaking with standard CMOS process. We report in this communication the surface modification of solgel derived (which is CMOS compatible) ZnO thin film by Pd using a very low concentration of $PdCl_2$ solution. The sensing temperature can be brought down to 150 °C from 250 °C by such modification. Our investigation further demonstrated that the response in lower (0.01 %) and higher (1.5 %) concentrations of methane is also better in case of Pd modified film possibly due to higher amount of adsorbed oxygen at Pd surface.

2. Experimental

Zinc oxide based thin film gas sensors were fabricated according to a method similar to the one reported earlier by us [5]. More precisely, for deposition of nanocrystalline ZnO films by sol-gel method, 0.45 molar Zinc acetate dihydrate [$Zn(CH_3COO)_2$-$2H_2O$] was used as the chemical precursor. (98 %) of 0.45 molar acetate was mixed with isopropanol a stirred well at room temperature. When the solution turned milky, diethanolamine (DEA) was added slowly to yield a clear transparent homogeneous solution. After aging for 24 h, the solution was subjected to spin coating on 0.6 μm thermally grown SiO_2 over p-Si (resistivity 1 Ω cm, 400 μm thick) substrates with a dimension 4 mm × 4 mm. The rotation speed of the coating unit was 1000 r.p.m and the duration of the single coating was 25 s. Then the samples were heated at 110^{o}C for 10 min to evaporate the solvent and to remove organic residuals. Finally the samples were annealed at 450^{o}C for producing nanocrystalline ZnO. The entire process was repeated for three times to produce a ZnO film of ~900 nm thickness. The detailed structural analysis e.g. X-Ray diffraction (XRD) measurements, Scanning Electron Microscopic (SEM) etc. of the nanocrystalline ZnO films produced by sol-gel method has been reported in our earlier publication [5].

The grown ZnO thin films were dipped into a 0.01M $PdCl_2$ solution for 2 s, 5 s and 10 s followed by baking and annealing at 110 ^{0}C for 10 min and 300 ^{0}C for 30 min, respectively. 5 s dipping was found to be optimum for sensor study. For 2 s dipping there was almost no improvement in sensor performance possibly due to very small amount of Pd dispersion, whereas for 10 s dipped samples the initial resistance of the sensor was very low due to excessive Pd island formation leading to poor

sensor performance. Field emission scanning electron microscopy (FESEM) (Fig 2 (a) and 2 (b)) and energy dispersive X-ray (JEOL, JSM-6700F) (Fig. 3) were employed to study the crystal size, surface morphology and pore size of the deposited ZnO thin films. FESEM pictures also demonstrate the nanocrystalline and nanoporous characters of the ZnO surface, both unmodified and modified with dispersed Pd nanoparticles.

The Pd–Ag (26 %) catalytic metal contact of thickness 0.2micron was deposited on the Pd modified ZnO thin films by e-beam evaporation (10^{-6} mbar) using an Al metal mask and the electrical contacts were taken by using fine copper wire and silver paste. The schematic of the resistive gas sensor structure with requisite dimensions is shown in Fig. 1.

The sensor characteristics were studied inside a closed corning glass tube (10 cm × 4 cmϕ) with inlet and outlet for gases and it was placed horizontally and coaxially inside a resistively heated furnace with a 4 cm constant temperature zone. The temperature was controlled within ±1°C using a copper constantan thermocouple in-built in a precise temperature controller. Electrical connections were taken by using fine copper wire and silver paste for the metallization contacts.

For sensor study high purity (100 %) methane gas and IOLAR grade N_2 in desired proportions were allowed to flow to the gas-sensing chamber through a mixing path via an Alicat Scientific (USA) mass flow controller and a mass flow meter for keeping the mass flow rate and thus the concentration of the methane gas constant throughout the experiments. The gas pressure over the sensor device was 1 atm during the experiments. The resistance of the sensors in presence and in absence of CH_4 was measured by a Keithley 6487 picoammeter /voltage source.

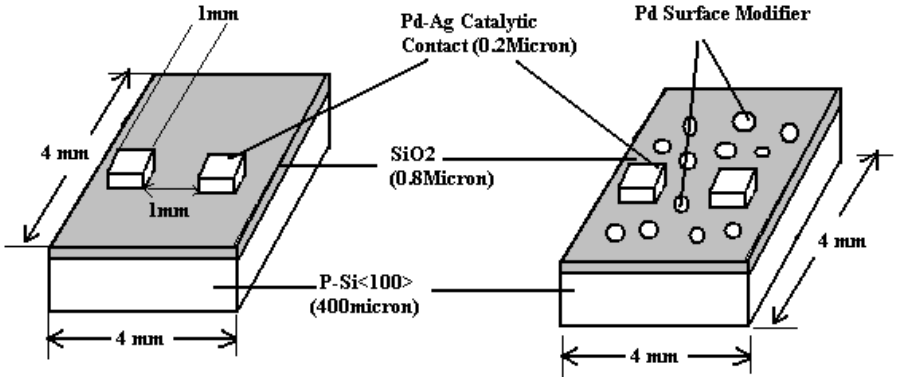
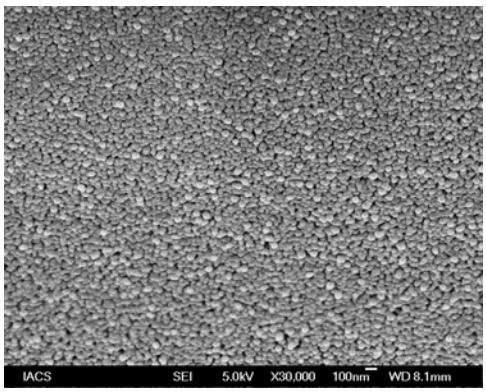


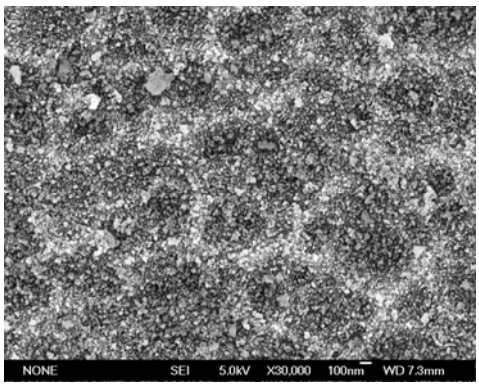
Fig. 1. Schematic of the unmodified and modified sensor structures with requisite dimensions.

3. Results and Discussions

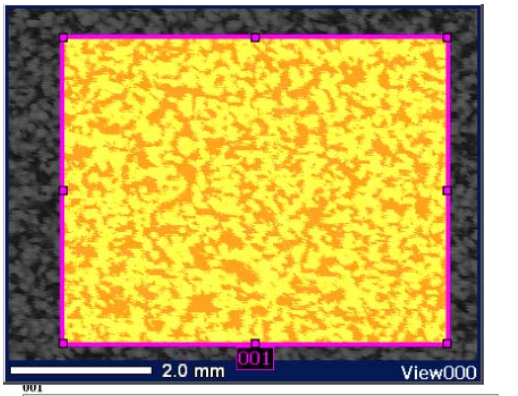
The FESEM images of the unmodified and Pd modified ZnO surface is shown in the Fig 2 (a) and 2 (b) respectively. From FESEM the surface morphology and the pore size were studied for both unmodified and modified ZnO surfaces, and it was observed that the pore size varied from 60 nm to 75nm for the unmodified ZnO surface and 40 nm to 50 nm for the modified one after treatment with the $PdCl_2$ solution (Fig. 2(a) and (b)). EDX (Fig. 2(c) and (d) figures indicate clearly the presence of Pd having a mass percentage of 4.7 dispersed uniformly over the entire ZnO surface. The table also indicates that the mass percentage of oxygen has been increased in the Pd modified film compared to its unmodified counterpart (from ~ 26 % to ~30 %). The probable cause may be the enhanced oxygen adsorption of dispersed Pd nanoparticles. The uniform dispersion of Pd nanoparticles is also supported by the X-Ray mapping of the modified ZnO film [Fig. 2(e)].



(a) FESEM image Unmodified ZnO.

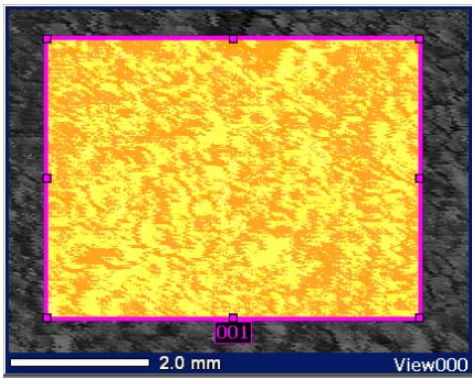


(b) FESEM image Pd modified ZnO.



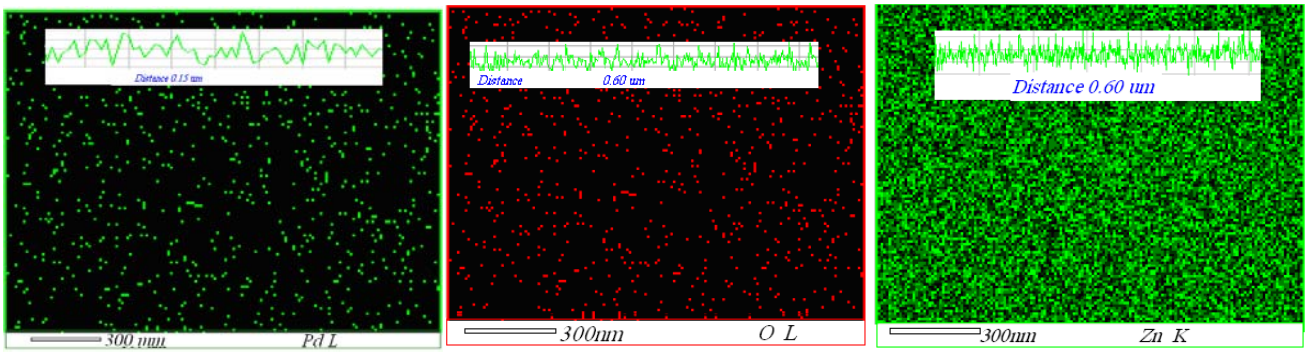
Ele...	(keV)	mass%	Error%	At%
O K	0.525	26.06	0.42	59.01
Zn K	8.630	73.94	1.28	40.99
Total		100.00		100.00

(c) EDX spectrum of unmodified ZnO.



Ele...	(keV)	mass%	Error%	At%
O K	0.525	30.29	0.18	64.58
Zn K	8.630	65.01	0.50	33.92
Pd L	2.838	4.70	0.24	1.51
Total		100.00		100.00

(d) EDX spectrum of Pd modified ZnO (5 Sec).



(e)

Fig. 2. FESEM images (a and b); EDX spectra of unmodified and Pd-modified ZnO thin films, respectively (c and d) and X-Ray Mapping of Pd modified ZnO (e).

The sensors were characterized with different concentrations of methane gas in pure nitrogen in the temperature range 100–350 °C. The resistance change of both types of sensor structures were studied at different temperatures and the magnitude of response (*S*) was calculated using the relation,

$$S = [Ra - Rg]/Rg,$$

where Ra = the resistance in air and Rg = the resistance in the presence of gas [5].

Fig 3(a) and (b) show the variation of response magnitude as a function of temperature both for as deposited and Pd modified sensors respectively. As revealed from the figure, for unmodified case the sensor showed no response to the lower concentrations like 0.01 % and 0.05 %. Moreover for the concentration higher than 1.0 % the response become saturated possibly due the occupancy of the all adsorption sites on the ZnO surface. For intermediate concentrations (0.1 % to 1.0 %) the sensor showed a maximum response at 250 °C. In contrast, for Pd modified sensors the peak response is obtained at around 150 °C. This is probably due to the well known catalytic effect of the dispersed Pd over ZnO surface. As the Pd modified surface offered higher amount of adsorption sites the modified structure showed appreciable response to very lower (0.01 %, 0.05 %) concentrations as well as to quite high concentration like 1.5 %. For Pd sensitized sensor the response become saturated above 1.5 % methane concentration due to capturing of all adsorption sites by the excessive number of methane molecules.

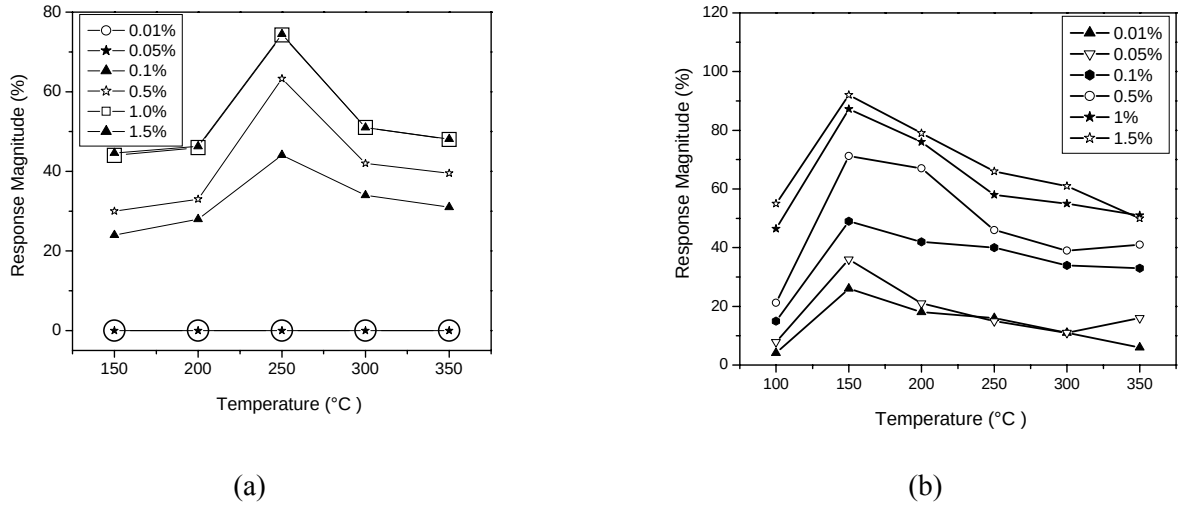
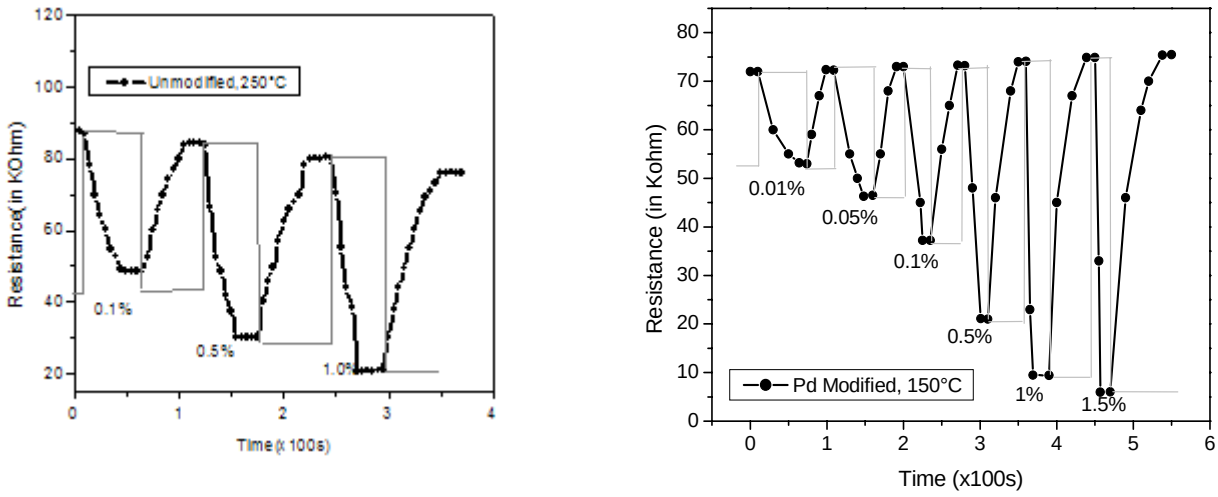


Fig. 3. Response magnitude of (a) unmodified and (b) Pd modified ZnO sensor as a function of temperatures for different methane concentrations.

Fig. 4 showed the dynamic response characteristic for unmodified and Pd modified sensors at their respective optimum temperatures (250 °C and 150 °C) whereas Table 1 and Table 2. depicts the response magnitude, response time and recovery time at five different gas concentrations and at different operating temperatures of unmodified and Pd modified Nano-ZnO sensor respectively. The response time and recovery time are much faster in case of Pd modified one due to the faster adsorption and desorption kinetics of the catalytic Pd. Upon exposure to methane the sensor resistance initially decreased due to the release of free electrons and then got saturated, while on cutting off the methane supply the resistance increased and returned nearly to its baseline value. Fig. 4 shows that they do not reach exactly the baseline value possibly because of some gas molecules remaining adsorbed on the sensor surface. The calculated values of response, response time and recovery time for

different gas concentrations are tabulated in Table 1 and Table 2, which shows that the values improve significantly with the Pd modification.



(a) (b)

Fig. 4. Dynamic response characteristics of (a) unmodified and (b) Pd modified ZnO sensor for different methane concentrations.

Table 1. Response magnitude, response time and recovery time at five different gas concentrations and at different operating temperatures of as deposit Nano-ZnO.

Temperature (°C)	**Response magnitude (%)**					
	0.01%	**0.05%**	**0.1%**	**0.5%**	**1%**	**1.5%**
100	---	---	---	---	---	---
150	---	---	24	30	44	44.6
200	---	---	28	33	46	46.3
250	---	---	**44.1**	**63.3**	**74.3**	**74.5**
300	---	---	34	42	51	51
350	---	---	31	39.5	48	48.1

Temperature (°C)	**Response Time (s)**					
	0.01%	**0.05%**	**0.1%**	**0.5%**	**1%**	**1.5%**
100	---	---	---	---	---	---
150	---	---	106	98	65	56
200	---	---	54	47	27	18
250	---	---	**22**	**20.1**	**16.3**	**14**
300	---	---	38	35	28	23
350	---	---	46	43	37	29

Temperature (°C)	**Recovery Time (s)**					
	0.01%	**0.05%**	**0.1%**	**0.5%**	**1%**	**1.5%**
100	---	---	---	---	---	---
150	---	---	122	129	146	159
200	---	---	76	88	92	107
250	---	---	**28**	**32.1**	**36.1**	**45**
300	---	---	44	47	56	66
350	---	---	53	58	64	78

Table 2. Response magnitude, response time and recovery time at five different gas concentrations and at different operating temperatures of Pd modified Nano-ZnO.

Temperature (°C)	**Response magnitude (%)**					
	0.01%	**0.05%**	**0.1%**	**0.5%**	**1%**	**1.5%**
100	4.1	7.9	15	21.2	46.4	55
150	**26**	**36**	**49**	**71.2**	**87.2**	**92**
200	18	21	42	67	76	79
250	16	15	40	46	58	66
300	11	11	34	39	55	61
350	6	16	33	41	51	50

Temperature (°C)	**Response Time (s)**					
	0.01%	**0.05%**	**0.1%**	**0.5%**	**1%**	**1.5%**
100	48	44	37	32	25	19
150	**36**	**26**	**17**	**14**	**6**	**5**
200	45	41	39	37	26	17
250	56	46	41	38	28	16
300	65	62	52	44	36	22
350	70	66	55	49	40	29

Temperature (°C)	**Recovery Time (s)**					
	0.01%	**0.05%**	**0.1%**	**0.5%**	**1%**	**1.5%**
100	29	38	42	55	61	77
150	**17**	**21**	**24**	**27**	**33**	**46**
200	24	36	40	51	59	67
250	25	39	45	55	64	70
300	36	43	50	59	69	80
350	112	124	134	145	151	160

Figs. 5 (a)-(c) show the bar chart for the response magnitude, response time and recovery time of the ZnO sensors without and with Pd modification at their respective optimum operating temperatures and at six different methane concentrations. For unmodified case the maximum response of 74 % was obtained and the minimum response and recovery time were found to be 16 s and 36 s in the presence of 1.0 % methane and at 250 °C. To the contrary with the same concentration of methane the maximum response of 87 % was obtained for Pd modified sensor at 150 °C, the minimum response and recovery time were found to be 6 s and 33 s (in 1.0 % methane), respectively.

As discussed in our earlier publication [8] the Pd modified nanocrystalline ZnO enhances the oxygen spillover process [9, 10], resulting in a large amount of chemisorbed oxygen which yields a high electrostatic potential across the Pd–Ag/ZnO Schottky interface [11]. Subsequently methane reacts with this adsorbed oxygen to produce H_2O and CO_2, following the Eq. (2) below

$$CH_4 + 2O_2^- \leftrightarrow CO_2 + 2H_2O + 4e^- \quad (2)$$

The electrons on the surface of ZnO enhance the current through the electrodes. The detailed mechanism of the gas sensing of Pd–Ag/ZnO Schottky contacts using electrochemically grown ZnO thin films was reported in our earlier publications [11]. Since the planar structure which has two-Schottky contacts with double barrier junctions and a large exposed surface area where oxygen atoms are directly chemisorbed, therefore the change of resistance in the presence of methane is relatively higher.

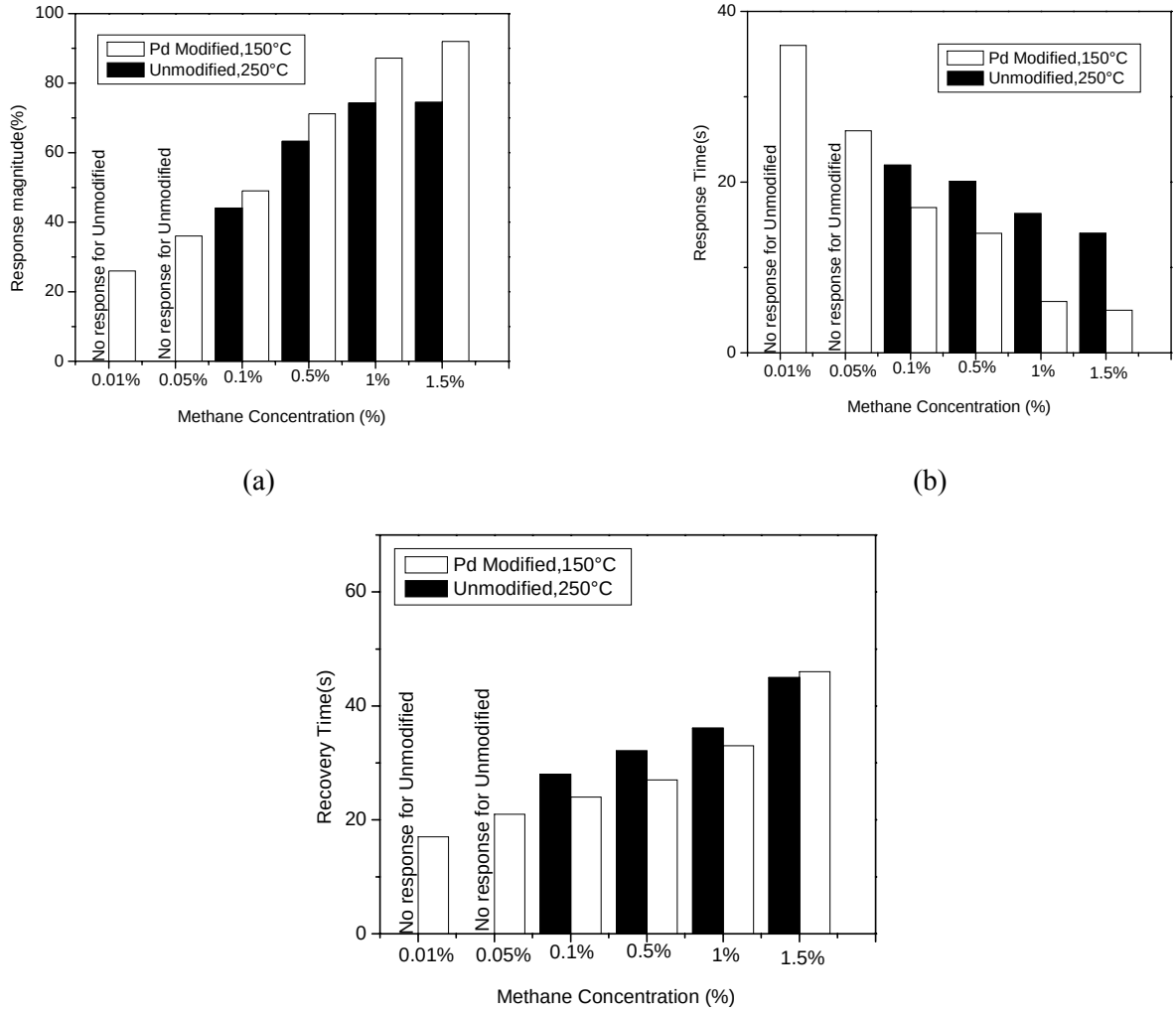


Fig. 5. Bar diagram showing: (a) response magnitude; (b) response time; (c) recovery time of unmodified and Pd modified ZnO sensor for six different methane concentrations.

The possible reason for the better response of Pd modified structure at substantially low temperature may be due to the increased surface free energy of the nanocrystalline ZnO surface [12]. It is known that with an increase in gas adsorption, the catalytic metal electrode (Pd) work function decreases, and the current through the Pd–ZnO Schottky junction increases, and thus the gas response increases [11]. Once the desorption starts at higher temperature, the change in work function decreases and the resistance in the presence of gas also increases leading to a poor response. In the planar configuration electrons would prefer to conduct from one electrode to other through the Pd modified ZnO surface, where Pd can assist relatively faster conductivity through possible hopping conduction mechanism from one island to other of discontinuously dispersed Pd. For nanocrystalline structure the adsorption activation energy is considerably low and the presence of dispersed Pd nanoparticles over the ZnO surface further reduces the adsorption energy. As a result the sensors respond at considerably low temperature. The favorable adsorption kinetics due to reduced adsorption activation energy also exhibits a remarkably fast time of response and recovery.

4. Conclusion

Surface modification of nanocrystalline– nanoporous ZnO thin films (deposited by sol-gel method) by Pd nanoparticles, using chemical dipping procedure, reduced the operating temperature and response time of methane sensing to an appreciably low value. For nanocrystalline structure the adsorption activation energy was considerably low and the presence of dispersed Pd nanoparticles acting as a catalyst over the ZnO surface further reduced the adsorption energy. As a result the sensors respond at considerably lower temperature. Moreover the modified surface was found to be more efficient in increasing the sensing range of the methane (from as low as 0.01 % to as high as 1.5 %) possibly due to higher amount of adsorbed oxygen on dispersed Pd surface.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

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Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

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- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
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- Nanosensors;
- Microsystems;
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